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(54) **DIFFERENT-SHRINKAGE COMPOSITE YARN AND PREPARATION METHOD THEREFOR**

(57) This invention relates to the different shrinkage composite yarn and its preparation method. The modified polyester is spun with a porous spinneret to produce a different shrinkage composite yarn, and the arrangement of the spinneret holes on the porous spinneret is arranged in an elliptical arrangement. That is, the spinning hole center of the spinneret is located on the concentric ellipse, the concentric ellipse is a series of ellipses, all the ellipses are long axis collinear, and short axis collinear. The different shrinkage composite yarn is obtained by winding modified polyester POY yarn and FDY yarn, net-

work recombining, and coiling them. The preparation method of modified polyester is as follows: terephthalic acid reacts with ethylene glycol to produce ethylene terephthalate. The modified polyester is obtained by the reaction of terephthalic acid with branched diol. The fiber of the invention has good properties and the deviation rate of fiber density. The CV value of breaking strength is $\leq 4.0\%$, the CV value of elongation at break is $\leq 8.0\%$, the CV value of coefficient of variation of coiling shrinkage is $\leq 8.0\%$.

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Description**TECHNICAL FIELD**

5 **[0001]** The invention relates to the field of polyester fiber and relates to a different shrinkage composite yarn and its preparation method.

BACKGROUND

10 **[0002]** Poly (ethylene terephthalate) (PET fiber or polyester fiber) fiber has high breaking strength and elastic modulus, moderate elasticity and excellent heat setting since it is invented. Heat resistance and light resistance, acid resistance, alkali resistance and corrosion resistance are a series of excellent properties, and the fabric has the advantages of crease resistance, ironing resistance, good fastness and so on. It is widely used in clothing, home textile and other fields.

15 **[0003]** However, because of the high crystallinity, dense structure and no functional groups on the molecular chain, the dye molecules are difficult to enter the fiber, and it is difficult to dye. Cannot meet people for bright and beautiful, unique style of fabric demand.

20 **[0004]** The reason for the difficulty of PET staining is that PET belongs to symmetrical straight chain macromolecules, the molecular chain does not contain side chain groups, and the regularity is very good. Its main chain contains rigid benzene ring and flexible hydrocarbon group. The ester group and benzene ring directly connected with the benzene ring form a rigid conjugate system, which restricts the free rotation of the flexible segment. This structure increases the wall and ridge of molecular chain motion, which leads to the higher glass transition temperature of PET. It is necessary to promote the diffusion of dye molecules to the fiber at very high temperature, and complete the dyeing process. In addition, the molecular chains of PET are regular, good crystallinity, tight arrangement of molecular chains, and there are no polar groups on the molecular chains that interact with dye molecules, which makes the coloring of PET fibers more difficult.

25 **[0005]** Therefore, the normal dyeing of PET fibers under high temperature and high pressure, the choice of disperse dyes dyeing, when the temperature of PET fiber to get glass transition temperature, PET fiber polymer molecule void increased, but its free volume increase is small. The dyeing rate is not high, but the energy consumption and the low dye uptake rate caused by the high temperature and high pressure method are the main problems now. In addition, the PET fiber is relatively high, which is not conducive to processing.

30 **[0006]** There are many methods for preparing PET fibers, among which melt spinning is one of the most widely used in industrial production. There are many parameters in the process of melt spinning. These parameters determine the forming process of the fiber and the structure and properties of the spun fiber. In production, the required properties are obtained by controlling these parameters. According to the technological process, the main spinning parameters controlled in production can be summarized as melting condition, spinneret condition, curing condition, winding condition, etc. Among them, the cooling and curing conditions of yarn strip have a decisive effect on the structure and properties of the fiber. In order to control the cooling rate and uniformity of polyester melt, cooling blowing is widely used in production. Cooling and blowing can accelerate the cooling rate of melt fine flow, which is helpful to increase the spinning speed, strengthen the convection of air around the yarn strip, make the inner and outer layer yarn strip cool evenly, and create conditions for the adoption of porous spinneret. Cooling and blowing can improve the quality of primary fiber and improve the tensile properties, which is beneficial to improve the production capacity of the equipment.

35 **[0007]** For a long time, chemical fiber production has been using side blowing as cooling method. Energy consumption accounts for a large part of the production cost of yarn. With the increasing demand for the properties and quality of chemical fiber, the development of the new product of chemical fiber yarn is developing towards the direction of high value-added differential fiber, which requires higher cooling and blowing conditions, so a ring blowing device is proposed. The ring blowing device not only has the advantage of uniform wind load per bundle, but also has low energy consumption, which effectively solves the problem of wind energy loss caused by the large blowing area.

40 **[0008]** In the spinning process, although the ring blowing has obvious advantages, there are still some problems: because the spun silk is extruded from the circular spinneret and cooled through the ring blowing, because the number of circular spinneret rings is more, This makes it difficult for the ring to blow into the innermost layer, causing the innermost silk to remain uncooled after the outermost silk has cooled, resulting in problems such as uneven fineness, uneven strength, uneven dyeing, and so on. As a result, the further processing of the silk may be difficult.

45 **[0009]** The different shrinkage composite yarn is a kind of yarn with different potential shrinkage properties, that is, the high shrinkage yarn POY and the low shrinkage yarn FDY are made by blending. The main features of the PET different shrinkage composite fiber are high swelling and soft handle. The appearance of PET different shrinkage composite yarn is similar to that of common yarn. The yarns with different potential shrinkage properties, that is, the composite yarn with high shrinkage POY and low shrinkage FDY, produced the effect of different shrinkage due to the difference of shrinkage rate between the two components.

SUMMARY

[0010] The purpose of the invention is to overcome the problems of dyeing irregularity and poor mechanical properties of the existing polyester fibers, to realize large-scale production spinning, and to provide a preparation method of the different shrinkage composite yarn. The raw material of the polyester fiber of the invention is modified polyester, the molecular chain of modified polyester is introduced into the chain of diol containing branched chain, the modified polyester fiber prepared by modified polyester, under certain temperature conditions, The space gap between molecular chains of modified polyester fibers is much larger than that of ordinary polyester fibers without branched chains at the same temperature, which is beneficial to the degree of tiny particles such as dye into the interior and to the higher dyeing rate. The melt viscosity of the modified polyester fiber is reduced, the processing temperature is reduced, and the degradation rate is reduced, which is beneficial to the processing. In addition, the structure regularity of the modified polyester fiber is not greatly damaged by the diol chain containing the branched chain. The excellent properties of polyester fiber are maintained. The spinning process of the invention adopts a spinneret arranged with a spinneret ellipse, which is advantageous to the uniform and sufficient cooling of the fiber during spinning, and the difference between the properties and structure of the fibers is relatively small, thus improving the dyeing uniformity and mechanical properties of the fibers.

[0011] In order to achieve the above purpose, the technical proposal of the invention is as follows:

This invention relates to a different shrinkage composite yarn, wherein the material of the different shrinkage composite yarn is a modified polyester, and the modified polyester is composed of a terephthalic acid chain, an ethylene glycol chain and a diol chain containing a branched chain. The branched diol segment locates on a non-terminal carbon in the diol chain segment and the branched chain is a diol chain segment containing a straight chain carbon chain of 5-10 carbon atoms.

[0012] The size of the different shrinkage composite yarn is 100-150 dtex. the breaking strength is ≥ 1.9 CN / dtex. the elongation at break is 30.0 ± 5.0 . At the temperature of 80°C - 130°C , the space gap between molecular chains in the fiber increased by 10-30v/v%. The deviation rate of fiber density of the different shrinkage composite yarn is $\leq 2.0\%$. The CV value of breaking strength is $\leq 4.0\%$, and the CV value of elongation at break is $\leq 8.0\%$, and the CV value of coiling shrinkage coefficient of variation is $\leq 8.0\%$, and crimp shrinkage is $3.50 \pm 2.0\%$, and the oil content is $1.0 \pm 0.2\%$, network 20 ± 5 units/m. The increase of the space gap between the molecular chains refers to the comparison of the spatial gaps between molecular chains at the same temperature between modified polyester and common polyester.

[0013] This invention also provides a preparation method of the different shrinkage composite yarn, wherein the modified polyester is spun from a porous spinneret to produce a different shrinkage composite yarn, and the arrangement of the spinneret holes in the porous spinneret is an elliptical arrangement. The elliptical arrangement means that the center of the spinning hole of the spinneret is located on the concentric ellipse, the concentric ellipse is a series of ellipses, the long axis collinear of all the ellipses, and the short axis collinear;

[0014] The preparation method of the different shrinkage composite yarn is as follows: The modified polyester POY yarn is prepared by metering, squeezing, cooling, oiling and winding the modified polyester, and the modified polyester FDY yarn is prepared by metering, extrusion, cooling, oiling, drawing, heat setting and winding the modified polyester chips. The modified polyester POY yarn and the modified polyester FDY yarn are combined as the network structure to form the different shrinkage composite yarn.

[0015] The preparation steps of the modified polyester are as follows:

(1) Preparation of terephthalic acid glycol ester:

Mix terephthalic acid and branched diol to slurry, and carry out the esterification reaction under the catalytic action of concentrated sulfuric acid to obtain a terephthalic acid glycol ester. The branched diol refers to a diol having a branched chain which is a non-terminal carbon in the diol segment and a branched chain having a linear carbon chain of 5 to 10 carbon atoms.

(2) Preparation of ethylene terephthalate:

Mix the terephthalic acid and the ethylene glycol to slurry, carry out the esterification reaction to obtain ethylene terephthalate.

(3) Preparation of modified polyester:

After the esterification reaction in the step (2) is completed, add the terephthalic acid glycol ester prepared in the step (1), stir and mix, run the polycondensation reaction under the action of the catalyst and the stabilizer, and under the condition of the negative pressure. First in a low vacuum stage and then in a high vacuum stage to obtain a modified polyester.

[0016] In the preparation methods of the different shrinkage composite yarn as put forward, the specific preparation steps of the modified polyester are as follows:

(1) Preparation of terephthalic acid glycol ester:

Add the slurry of the terephthalic acid and the branched diol to the reactor, and carry out the esterification reaction under the catalytic action of concentrated sulfuric acid. The esterification reaction is carried out under a pressurized nitrogen environment, and the pressure is normal pressure to 0.3 MPa, and the temperature is 180-240 °C. The reaction ends when the water distillation amount in the esterification reaction reaches 90% of the theoretical value or more than that. Then the terephthalic acid glycol ester is obtained.

(2) Preparation of ethylene terephthalate:

Add the slurry of the terephthalic acid and ethylene glycol into a reactor and then carry out the esterification reaction. The esterification reaction is carried out under a pressurized nitrogen environment, and the pressure is normal pressure to 0.3 MPa, and the temperature is 250-260 °C. The reaction ends when the water distillation amount in the esterification reaction reaches 90% of the theoretical value or more than that. Then the ethylene terephthalate is obtained.

(3) Preparation of modified polyester:

After the end of the esterification reaction in the step (2), add the terephthalic acid glycol ester prepared in the step (1), stir and mix for 15-20 minutes under the action of the catalyst and the stabilizer, and a negative pressure. Carry out the polycondensation reaction under the condition of the low-vacuum stage, the pressure is smoothly pumped from normal pressure to an absolute pressure under 500Pa, the temperature is controlled at 260~270°C, and the reaction time is 30~50 minutes. Then turn to high vacuum stage, the polycondensation reaction continues and the reaction pressure is reduced to an absolute pressure of less than 100 Pa, and the reaction temperature is controlled at 275 to 280 °C, and the reaction time is 50 to 90 minutes in order to obtain a modified polyester.

[0017] The main spinning process parameters of the different shrinkage composite yarn are as follows:

Spinning temperature: 280-300°C;
Wind temperature: 20-22 °C;
Network pressure of joint stock: 3.5-4.5bar.
GR1 speed: 800-1000m/min;
SR1 speed: 3000-4200m/min;
GR2 speed: 3000-4000m/min;
HT1 temperature: 90-115°C;
HT2 temperature: 130-140°C;
Winding speed: 3000-4000m/min.

[0018] In the preparation methods of the different shrinkage composite yarn as put forward, in step (1), the molar ratio of terephthalic acid to branched diol is 1: 1.3-1.5%. The amount of concentrated sulfuric acid added is 0.3-0.5% of the weight of terephthalic acid; The concentration of concentrated sulfuric acid is 50-60 wt%;

[0019] In step (2), the molar ratio of terephthalic acid to ethylene glycol is 1: 1.2-2.0;

[0020] In step (3), the molar percentage value of the diol terephthalate and ethylene terephthalate is 2-5%; the catalyst is antimony trioxide, antimony glycol or antimony acetate, and the amount of catalyst added is 0.01%-0.05% of the total weight of terephthalic acid; The stabilizer is triphenyl phosphate, trimethyl phosphate or trimethyl phosphite, and the amount of stabilizer added is 0.01%-0.05% of the total weight of terephthalic acid;

[0021] The number average molecular weight of the modified polyester is 15000-30000.

[0022] In the preparation methods of the different shrinkage composite yarn as put forward the branched diol is one or more items selected from the group consisting of a 2-pentyl-1,3 propanediol, a 2-hexyl-1,3 propanediol, a 2-heptyl-1,3 propanediol, a 2-octyl-1,3 propanediol, a 2-mercapto-1,3 propanediol, a 2-mercapto group-1,3 propanediol, a 2-pentyl-1,4 butanediol, a 2-hexyl-1,4 butanediol, a 2-heptyl-1,4 butanediol, a 2-octyl-1,4 butanediol, a 2-mercapto-1,4 butanediol, a 2-mercapto-1,4 butanediol, a 2-pentyl-1,5 pentanediol, a 2-hexyl-1,5-pentanediol, a 2-heptyl-1,5-pentanediol, a 2-octyl-1,5-pentanediol, a 2-mercapto group-1,5 pentanediol glycol, a 2-mercapto-1,5 pentanediol, a 2-pentyl-1,6 hexanediol segment, a 2-hexyl-1,6 hexanediol, a 2-heptyl-1,6-hexanediol, a 2-octyl-1,6-hexanediol, a 2-mercapto-1,6-hexanediol and a 2-mercapto-1,6 hexanediol.

[0023] In the preparation methods of the different shrinkage composite yarn as put forward, the arrangement of the spinneret holes is long axis and/or short axis symmetry.

[0024] In the preparation methods of the different shrinkage composite yarn as put forward, the ratio of the long axis of the ellipse to the length of the short axis is 1.3-1.8; the spacing of the adjacent spinneret holes is greater than the diameter of the guide hole equal to the diameter of the guide hole of the spinneret hole plus 1.5mm.

[0025] In the preparation methods of the different shrinkage composite yarn as put forward, the spinneret is a circular spinneret or an elliptical spinneret. The difference between the diameter of the circular spinneret and the maximum length of the long axis of the series ellipse is greater than 10 mm, and the difference value between the elliptical spinneret and the maximum length of the long axis of the series ellipse is greater than 10mm.

[0026] In the preparation methods of the different shrinkage composite yarn as put forward, the guide hole diameter of the spinneret is 1.5-2.5mm; the number of spinneret holes is greater than or equal to 192.

[0027] In the preparation methods of the different shrinkage composite yarn as put forward, the cross-section shape of the spinneret spinning hole is one kind of circular, square, diamond, one font, triangular, trilobal, hollow or flat.

[0028] The principle of the invention is:

For polyester fibers without branched chains, the molecular chain structure is a linear macromolecule with benzene ring structure, the functional groups on the molecular chain are arranged neatly, the regularity is good, the flexibility is poor, and the free volume increase is small when the temperature increases. These properties prevent the dye from entering the polyester fiber, so the dyeing performance is poor.

[0029] The raw material of the polyester fiber of the invention is a modified polyester. The modified polyester macromolecule contains a segment of diol containing a branched chain. When the temperature is higher than the glass transition temperature, the branching chain moves before the main chain. The increase of free volume is much larger than that of polyester macromolecular chain without branched chain, and the increase of free volume increases the degree of tiny particles entering into the polyester. The free volume of polyester fiber prepared by modified polyester is much larger than that of polyester fiber without branched chain at the same temperature, which increases the degree of dye diffusion and improves the dyeing performance of polyester fiber. At the same time, the polyester fiber prepared by modified polyester can reduce the melt viscosity and improve its processability. The structure regularity of polyester fiber is not destroyed by the introduction of diol chain with branched chain, and the excellent properties of polyester fiber are maintained.

[0030] When the effective area of spinneret is the same, because the circumference of ellipse is larger than that of circle, the number of layers in elliptical arrangement of spinneret is smaller than that in circular arrangement, and the number of holes in elliptical arrangement of spinneret is larger than that in circular arrangement. The spinneret with spinneret elliptical arrangement can make the fiber cool quickly and uniformly, and the difference between the structure and properties of the fibers is small, which is helpful to improve the dyeing uniformity of the fibers and the properties of the fibers.

[0031] Benefits:

(1) When the effective area of the spinneret is the same, the number of layers arranged in the elliptical arrangement of the spinneret is smaller than the number of layers arranged in the circle, and the ring blowing is easier to blow through the spinning flow. The cooling effect of spinning flow is better and the properties of the prepared fibers are better.

(2) When the effective area of the spinneret is the same, the number of holes arranged in the elliptical arrangement of the spinneret is larger than that in the circular arrangement, and the elliptical arrangement can achieve greater cooling. The cooling efficiency is improved significantly.

(3) The material of the different shrinkage composite yarn is a modified polyester. The modified polyester macromolecule contains a segment of diol containing a branched chain. When the temperature is higher than the glass transition temperature, the branching chain moves before the main chain. The increase of free volume is much larger than that of polyester macromolecular chain without branched chain, and the increase of free volume increases the degree of tiny particles entering into the polyester. The free volume of polyester fiber is increased by branching chain to increase the degree of dye diffusion and the dyeing property of polyester fiber is improved.

(4) The polyester fiber free volume increase is conducive to reducing melt viscosity and improving its processing performance.

(5) The different shrinkage composite yarn prepared by the invention has no great damage to the structure regularity of the polyester fiber by introducing the diol chain segment containing the branched chain, and the excellent performance of the polyester fiber is maintained.

(6) The dyed and mechanical properties of the different shrinkage composite yarn are excellent, the fiber density deviation rate of the different shrinkage composite yarn is $\leq 2.0\%$, the CV value of breaking strength is $\leq 4.0\%$, the CV value breaking elongation is $\leq 8.0\%$ and the CV value of coiling shrinkage variation coefficient is $\leq 8.0\%$.

BRIEF DESCRIPTION OF THE DRAWINGS

[0032]

Fig. 1 is an elliptical arrangement of 374 spinneret holes with an aperture of 2.0 mm and a length ratio of 1.3 mm between the long axis and the short axis of the ellipse;

Fig. 2 is a circular arrangement of 370 spinneret holes with an aperture of 2.0 mm;

Fig. 3 shows the elliptical arrangement of 382 spinneret holes with an aperture of 2.0 mm and a length ratio of 1.6 for the long and short axes of the ellipse.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0033] Hereinafter, the present invention will be described in more detail by the following examples. It should be noticed that these examples are only for illustrating the present invention and are not intended to limit the scope of the present invention. In addition, it should be noticed that after reading the content of the present invention, those skilled in this field can make various modifications or changes to the present invention, and these equivalent forms also apply to the scope of the appended Claims of this application.

EXAMPLES 1~ 28

[0034] A preparation method of a modified polyester, including the following steps:

(1) Preparation of terephthalic acid glycol esters:

Add the terephthalic acid and *B* at a molar ratio of *A* as a mixture into the reactor at a concentration of *Cwt%*, and the amount added is *D%* by weight of terephthalic acid. Under the catalysis of sulfuric acid, the esterification reaction is carried out. The esterification reaction is pressurized to *E* MPa under a nitrogen environment, the pressure is normal pressure, the temperature is *F*°C. The esterification reaction ends until the water distillation amount in the esterification reaction reaches *G%* of the theoretical value, and the terephthalic acid glycol ester is obtained.

(2) Preparation of ethylene terephthalate:

The terephthalic acid and ethylene glycol having a molar ratio of *H* are mixed into the reactor, and then the esterification reaction is carried out. The esterification reaction is pressurized to *I* MPa under a nitrogen environment, and a temperature of *F*°C. When the water distillation amount in the esterification reaction reaches *K%* of the theoretical value, the esterification reaction ends, and ethylene terephthalate is obtained;

(3) Preparation of modified polyester:

Add the terephthalate diol phthalate ester diol prepared in step(1) after completion of the esterification reaction in step(2). The molar percentage of terephthalate diol phthalate ester diol and ethylene glycol terephthalate is of *L%*. Stir and mix for *M* minutes. Add *N%* of *O* as catalyst in a total amount of terephthalic acid and *P%* of *Q* as stabilizer in a total amount of terephthalic acid. The polycondensation reaction in the low vacuum phase is started under the condition of negative pressure. The pressure is smoothly pumped from atmospheric pressure to an absolute pressure of *R* Pa, the temperature is controlled at *S* °C, and the reaction time is *T* minutes, then the vacuum is continued for the high vacuum phase. The polycondensation reaction is carried out to reduce the reaction pressure to an absolute pressure of *U* Pa, the reaction temperature is controlled at *V* °C, and the reaction time is *W* minutes. Then we can obtain the modified polyester.

[0035] The modified polyester obtained has a number average molecular weight of *X* and consists of terephthalic acid segment, ethylene glycol segment and branched *B* segment. The molar percentage of branched *B* segment and the ethylene glycol segment is *Y%*.

[0036] The parameters of the variation in the different examples are shown in the following table. In the table, "BA" stands for 2-pentyl-1,3 propanediol, "BB" stands for 2-hexyl-1,3 propanediol, and "BC" stands for 2-Heptyl-1,3 propanediol, "BD" stands for 2-octyl-1,3 propanediol, "BE" stands for 2-mercapto-1,3 propanediol, and "BF" stands for 2-mercapto-1, 3 propylene glycol, "BG" stands for 2-pentyl-1,4 butanediol, "BH" stands for 2-hexyl-1,4 butanediol, and "BI" stands for 2-heptyl-1,4 The diol, "BJ" stands for 2-octyl-1,4 butanediol, "BK" stands for 2-mercapto-1,4 butanediol, and "BL" stands for 2-mercapto-1,4 Butanediol, "BM" stands for 2-pentyl-1,5-pentanediol, "BN" stands for 2-hexyl-1,5-pentanediol, and "BO" stands for 2-heptyl-1,5 Pentyl glycol, "BP" stands for 2-octyl-1,5 pentanediol, "BQ" stands for 2-mercapto-1,5 pentanediol, and "BR" stands for 2-mercapto-1.5 pentanediol, "BS" represents 2-pentyl-1,6 hexanediol, "BT" represents 2-hexyl-1, 6 hexanediol, and "BU" represents 2-heptyl-1, 6 hexanediol, "BV" stands for 2-octyl-1,6 hexanediol, "BW" stands for 2 - mercapto-1,6-hexanediol, "BX" represents 2-mercapto-1,6-hexanediol, "OA" stands for antimony trioxide, "OB" stands for ethylene glycol, and "OC" stands for Barium acetate, "QA" stands for triphenyl phosphate, "QB" stands for trimethyl phosphite, and "QC" stands for trimethyl phosphite, and the ratio is molar ratio.

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Table 1: parameters of the variation in the different examples

E X A M P L E	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y
1	1:1.3	BA	50	0.3	0.1	18 0	90	1:1.2	0.1	250	90	2	15	0.0 1	O A	0.0 1	Q A	500	2 6 0	3 0	1 0 0	2 7 5	5 0	1 5 0 0 0	2
2	1:1.3 8	BB	55	0.32	0.13	18 1	91	1:1.3	0.1 2	251	91	2.1	16	0.0 11	O A	0.0 2	Q A	490	2 6 2	3 1	9 9	2 7 6	5 1	1 6 0 0 0	2.1
3	1:1.3 3	BC	55	0.33	0.12	18 3	92	1:1.3 1	0.3 1	252	92	2.2	16	0.0 3	O A	0.0 2	Q A	498	2 6 3	3 2	8 0	2 7 7	5 7	1 5 9 0 0	2.2
4	1:1.3 4	BD	60	0.34	0.13	18 4	93	1:1.3 2	0.3 3	253	93	2.3	17	0.0 33	O A	0.0 23	Q A	497	2 6 4	3 3	8 0	2 7 8	5 8	1 5 8 0 0	2.3
5	1:1.3 5	BE	55	0.36	0.14	18 5	93 2	1:1.3 3	0.1 4	254	93. 2	2.4	17	0.0 34	O A	0.0 24	Q A	496	2 6 5	3 4	7 0	2 7 7	5 9	1 5 9 0 0	2.4

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5	6	1:1.3 6	BF	50	0.37	0.15	18 6	93 3	1:1.3 4	0.1 5	255	93. 3	2.5	18	0.0 35	O A	0.0 25	Q A	495	2 6 6	3 5	7 0	2 7 8	6 0	1 6 0 0 0	2.5
10	7	1:1.3 7	BG	60	0.38	0.16	18 7	93 4	1:1.3 6	0.1 6	256	93. 4	2.6	19	0.0 36	O A	0.0 25	Q A	496	2 6 7	3 6	7 0	2 7 8	6 1	1 6 0 0 0	2.6
15	8	1:1.3 8	BH	55	0.39	0.17	18 8	93 5	1:1.3 7	0.1 7	257	93. 5	2.7	19	0.0 36	O A	0.0 25	Q A	496	2 6 7	3 6	6 0	2 7 8	6 1	1 7 0 0 0	2.7
20	9	1:1.3 9	BI	50	0.4	0.17	18 8	93 5	1:1.3 7	0.1 7	257	93. 5	2.8	16	0.0 4	O B	0.0 26	Q B	497	2 6 8	3 8	5 0	2 7 9	6 2	1 8 0 0 0	2.8
25	10	1:1.4	BJ	55	0.4	0.17	18 8	93 5	1:1.3 8	0.1 8	257. 8	93. 6	3	17	0.0 3	O B	0.0 27	Q B	498	2 6 9	3 9	5 0	2 7 8	6 4	1 9 0 0 0	3
30	11	1:1.4	BK	55	0.4	0.18	18 9	93 6	1:1.3 9	0.1 9	258. 8	94	4	18	0.0 4	O B	0.0 3	Q B	497	2 6 0	4 0	4 0	2 7 7	6 3	2 0 0 0 0	4
35	12	1:1.4	BL	55	0.4	0.2	20 0	94	1:1.6	0.2	256	94	4.5	18	0.0 38	O C	0.0 3	Q C	497	2 6 5	4 2	4 0	2 7 7	7 0	2 6 0 0 0	4
40	13	1:1.5	BM	60	0.5	0.3	24 0	92	1:2.0	0.3	260	92	5	20	0.0 5	O C	0.0 5	Q C	450	2 7 0	5 0	3 0	2 8 0	9 0	3 0 0 0 0	5
45	14	1:1.4 7	BN	60	0.47	0.28	22 0	92	1:1.8	0.2 7	258	92	4	18	0.0 4	O B	0.0 4	Q B	460	2 6 3	4 7	4 0	2 7 8	8 5	2 8 0 0 0	4
50	15	1:1.4 6	BO	60	0.49	0.28	23 3	92	1:1.8	0.2 8	259	92	4.5	19	0.0 44	O A	0.0 46	Q A	490	2 6 9	4 8	4 0	2 7 9	8 7	2 9 0 0 0	4.5
55	16	1:1.4 9	BP	60	0.48	0.28	23 0	92	1:1.8	0.2 8	258	92	4.7	19	0.0 48	O B	0.0 47	Q A	460	2 6 7	4 8	4 0	2 7 9	8 3	2 7 0 0 0	4.7

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5	17	1:1.4 67	BQ	60	0.47	0.27	23 6	92	1:1.8 9	0.2 8	258	92	4.3	18	0.0 4	O A	0.0 41	Q C	490	2 6 8	4 8	4 0	2 7 8	8 5	2 9 0 0 0	4.3
10	18	1:1.4 8	BR	55	0.46	0.28	23 0	92	1:1.8 8	0.2 8	256	92	4.7	18	0.0 47	O A	0.0 47	Q A	480	2 6 5	4 7	4 0	2 7 9	8 5	2 8 0 0 0	4.7
15	19	1:1.4 6	BS	55	0.47	0.28	23 8	92	1:1.9	0.2 8	259	92	4.7	19	0.0 46	O C	0.0 48	Q C	446	2 6 7	4 9	4 0	2 7 8	8 7	2 9 0 0 0	4.7
20	20	1:1.4 6	BT	60	0.46	0.26	22 1	92	1:1.8 9	0.2 5	259	92	4.1	18	0.0 41	O B	0.0 42	Q B	460	2 6 5	4 7	4 0	2 7 8	8 5	2 8 0 0 0	4.1
25	21	1:1.4 3	BU	60	0.47	0.27	23 5	92	1:1.7 8	0.2 6	255	92	4.3	17	0.0 43	O A	0.0 49	Q A	490	2 6 8	4 6	4 0	2 7 5	8 5	2 8 0 0 0	4.3
30	22	1:1.4 3	BV	55	0.45	0.29	23 5	92	1:1.8 7	0.2 7	255	92	4.6	18	0.0 47	O B	0.0 4	Q A	470	2 6 8	4 5	4 0	2 7 9	8 3	2 9 0 0 0	4.6
35	23	1:1.4 57	BW	55	0.46	0.28	23 9	92	1:1.8 1	0.2 7	255	92	4.4 1	19	0.0 42	O A	0.0 48	Q C	495	2 6 5	4 5	5 0	2 7 5	8 5	2 8 0 0 0	4.4 1
40	24	1:1.4 7	BX	55	0.48	0.27	24 5	92	1:1.8 1	0.2 7	259	92	4.6 7	19	0.0 41	O A	0.0 42	Q A	485	2 6 8	4 6	5 0	2 7 5	8 9	2 9 0 0 0	4.6 7
45	25	1:1.4 5	BW +B G(3: 1)	55	0.49	0.26	23 6	92	1:1.8	0.2 8	258	92	4.4	18	0.0 42	O A	0.0 47	Q C	495	2 6 5	4 9	5 0	2 7 8	8 8	2 9 0 0 0	4.4
50	26	1:1.4 5	BO +B X(3: 2)	60	0.45	0.28	23 9	92	1:1.8 4	0.2 9	255	92	4.6	18	0.0 42 3	O A	0.0 45	Q C	495	2 6 5	4 5	5 0	2 7 8	8 5	2 8 0 0 0	4.6
55	27	1:1.4 5	BW +B G(3: 1)	55	0.49	0.26	23 6	96	1:1.8	0.2 8	258	92	4.4	18	0.0 42	O A	0.0 47	Q C	495	2 6 5	4 9	5 0	2 7 8	8 8	2 9 0 0 0	4.4
	28	1:1.4 5	BD +B G+ BQ(3: 2: 1)	60	0.47	0.29	23 5	92	1:1.8	0.2 7	258	92	4.7 1	18	0.0 4	O A	0.0 41	Q C	490	2 6 8	4 9	5 0	2 7 7	8 4	2 9 0 0 0	4.7 1

EXAMPLE 29

[0037] The invention relates to a preparation method of different shrinkage composite yarn, which is made from a porous spinneret. The arrangement of holes on the spinneret is elliptical, which means that the spinning hole center of the spinneret is located on a concentric ellipse. Concentric ellipse is a series of ellipses, all ellipses of the long axis collinear, and short axis collinear.

[0038] As shown in fig.1, the ratio of the length of the long axis to the short axis of the ellipse is 1.3, the spacing of the adjacent spinneret is equal to the diameter of the guide hole of the spinneret plus 1.5 mm, and the spinneret is a circular spinneret. The difference between the diameter of the circular spinneret and the maximum length of the long axis of the series is 11mm, the diameter of the spinneret is 2.0mm, the number of spinneret holes is 374, and the cross section shape of the spinneret spinning hole is circle.

[0039] The modified polyester POY yarn is prepared by metering, squeezing, cooling, oiling and winding the modified polyester prepared in EXAMPLE 1, and the modified polyester FDY yarn is prepared by metering, extrusion, cooling, oiling, drawing, heat setting and winding the modified polyester chips. The modified polyester POY yarn and the modified polyester FDY yarn are combined as the network structure to form the different shrinkage composite yarn. The main spinning process parameters are: spinning temperature 280°C, wind temperature 20 °C, combined network pressure 3.5 bar, GR1 speed 1000m/min, SR1 speed 4000m/min, GR2 speed 3000m/min, HT1 temperature 100°C, HT2 temperature 130°C, winding speed 3000m/min.

[0040] The size of the different shrinkage composite yarn is 120tex, and the breaking strength of the yarn is 2.7 cN/dtex, the elongation at break is 30.7%, and the curling shrinkage rate is 4.53%, and network degree is 25units/m. At the temperature of 80°C, the space gap between molecular chains of the different shrinkage composite yarn is increased by 15v/v%. The fiber density deviation rate is 1.7%, the CV value of the breaking strength is 3.2%, the CV value of elongation at break is 6.9%, the CV value of coiling shrinkage variation coefficient is 7.2% and the oil content is 1.0%.

EXAMPLE 30

[0041] The invention relates to a preparation method of different shrinkage composite yarn, which is made from a porous spinneret. The arrangement of holes on the spinneret is elliptical, which means that the spinning hole center of the spinneret is located on a concentric ellipse. Concentric ellipse is a series of ellipses, all ellipses of the long axis collinear, and short axis collinear.

[0042] As shown in fig.3, the ratio of the length of the long axis to the short axis of the ellipse is 1.6, the spacing of the adjacent spinneret is equal to the diameter of the guide hole of the spinneret plus 1.5 mm, and the spinneret is a circular spinneret. The difference between the diameter of the circular spinneret and the maximum length of the long axis of the series is 11mm, the diameter of the spinneret is 2.0mm, the number of spinneret holes is 382, and the cross section shape of the spinneret spinning hole is circle.

[0043] The modified polyester POY yarn is prepared by metering, squeezing, cooling, oiling and winding the modified polyester prepared in EXAMPLE 1, and the modified polyester FDY yarn is prepared by metering, extrusion, cooling, oiling, drawing, heat setting and winding the modified polyester chips. The modified polyester POY yarn and the modified polyester FDY yarn are combined as the network structure to form the different shrinkage composite yarn. The main spinning process parameters are: spinning temperature 280°C, wind temperature 20 °C, combined network pressure 3.5 bar, GR1 speed 1000m/min, SR1 speed 4000m/min, GR2 speed 3000m/min, HT1 temperature 100°C, HT2 temperature 130°C, winding speed 3000m/min.

[0044] The size of the different shrinkage composite yarn is 100tex, and the breaking strength of the yarn is 3.0 cN/dtex, the elongation at break is 35%, and the curling shrinkage rate is 4.77%, and network degree is 25units/m. At the temperature of 80°C, the space gap between molecular chains of the different shrinkage composite yarn is increased by 15v/v%. The fiber density deviation rate is 1.5%, the CV value of the breaking strength is 3.1%, the CV value of elongation at break is 5.3%, the CV value of coiling shrinkage variation coefficient is 4.9% and the oil content is 1.2%.

COMPARATIVE EXAMPLE 1

[0045] The invention relates to a preparation method of different shrinkage composite yarn, which is made from a porous spinneret. The arrangement of holes on the spinneret is circular, which means that the spinning hole center of the spinneret is located on a concentric circle. Concentric circle is a series of circles.

[0046] As shown in fig.2, the spacing of the adjacent spinneret is equal to the diameter of the guide hole of the spinneret plus 1.5 mm, and the spinneret is a circular spinneret. The difference between the diameter of the circular spinneret and the maximum diameter of the circle in the series is 11mm, the diameter of the spinneret is 2.0mm, the number of spinneret holes is 370, and the cross section shape of the spinneret spinning hole is circle.

[0047] The modified polyester POY yarn is prepared by metering, squeezing, cooling, oiling and winding the modified

polyester prepared in EXAMPLE 1, and the modified polyester FDY yarn is prepared by metering, extrusion, cooling, oiling, drawing, heat setting and winding the modified polyester chips. The modified polyester POY yarn and the modified polyester FDY yarn are combined as the network structure to form the different shrinkage composite yarn. The main spinning process parameters are: spinning temperature 280°C, wind temperature 20 °C, combined network pressure 3.5 bar, GR1 speed 1000m/min, SR1 speed 4000m/min, GR2 speed 3000m/min, HT1 temperature 100°C, HT2 temperature 130°C, winding speed 3000m/min.

[0048] The size of the different shrinkage composite yarn is 150tex, and the breaking strength of the yarn is 1.8 cN/dtex, the elongation at break is 25%, and the curling shrinkage rate is 5.6%, and network degree is 17units/m. At the temperature of 80°C, the space gap between molecular chains of the different shrinkage composite yarn is increased by 15v/v%. The fiber density deviation rate is 2.6%, the CV value of the breaking strength is 4.5%, the CV value of elongation at break is 8.2%, the CV value of coiling shrinkage variation coefficient is 8.5% and the oil content is 1.2%.

[0049] Comparing with Example 29, it can be seen that when the effective areas of the spinnerets are the same, and the number of spinning holes is similar (the number of spinning holes arranged in a circular array is 370, the number of spinning holes in an elliptical arrangement is 374, the number of layers of the spinning holes in elliptical arrangement is 6, which is smaller than the number(8) of the layers of spinning hole in circular arrangement, making the cooling effect better. Compared with the EXAMPLE 30, it can be seen that when the effective areas of the spinnerets are the same, the spinning holes are arranged in an elliptical shape, and the number of the layers of spinning holes in elliptical arrangement is 5, which is smaller than the circular arrangement of layers 8, making better cooling effect. The number(382) of holes of spinneret spinning hole elliptical arrangement is larger than the number(370) of spinning holes in circular arrangement, making higher cooling efficiency. Compared to the fiber properties in EXAMPLE 29 and EXAMPLE 30, the fiber density variation, the CV value of breaking strength, the CV value of elongation at break, the CV value of yarn unevenness of the fiber in EXAMPLE 29 and EXAMPLE 30 is smaller than Comparative Example 1, proving that under the same condition, the performance of the fiber made by the spinneret having the elliptical arrangement of the spinning holes is superior to that of the spinneret which is arranged in a circular shape.

EXAMPLE 31-33

[0050] The invention relates to a preparation method of different shrinkage composite yarn, which is made from a porous spinneret. The arrangement of holes on the spinneret is elliptical, which means that the spinning hole center of the spinneret is located on a concentric ellipse. Concentric ellipse is a series of ellipses, all ellipses of the long axis collinear, and short axis collinear.

[0051] The arrangement of the orifices is long axis symmetry. The ratio of the length of the long axis to the short axis of the ellipse is 1.4, the spacing of the adjacent spinneret is equal to the diameter of the guide hole of the spinneret plus 1.6 mm, and the spinneret is a circular spinneret. The difference between the diameter of the circular spinneret and the maximum length of the long axis of the series is 12mm, the diameter of the spinneret is 1.5mm, the number of spinneret holes is 192, and the cross-section shape of the spinneret spinning hole is square.

[0052] The modified polyester POY yarn is prepared by metering, squeezing, cooling, oiling and winding the modified polyester, and the modified polyester FDY yarn is prepared by metering, extrusion, cooling, oiling, drawing, heat setting and winding the modified polyester chips. The modified polyester POY yarn and the modified polyester FDY yarn are combined as the network structure to form the different shrinkage composite yarn. The main spinning process parameters are: spinning temperature 300°C, wind temperature 21 °C, combined network pressure 4.5bar, GR1 speed 800m/min, SR1 speed 3000m/min, GR2 speed 4000m/min, HT1 temperature 90°C, HT2 temperature 140°C, winding speed 4000m/min and the oil content of the different shrinkage composite yarn is 0.8%-0.9%. At the temperature of 80°C, the increasing rate of the space gap between the molecular chain inside the fiber and the data of mechanical properties of the fiber is:

Table 2: the different shrinkage composite yarn's mechanical properties when use the polyester from EXAMPLE 2 to EXAMPLE 4

EXAMPLE	Modified polyester source	Breaking strength (cN/dtex)	Elongation at break (%)	Increased gap (v/v%)	Fiber density deviation rate (%)	CV value of breaking strength (%)	CV value of elongation at break (%)	CV value of curl shrinkage coefficient of variation (%)	Network degree (pieces/m)	Curl shrinkage rate (%)	Denier (dtex)
31	Example 2	2.0	27.0	15	2.0	4.0	8.0	7.6	20	3.7	110
32	Example 3	2.4	28.0	15	1.7	3.8	7.6	8.0	22	3.9	100
33	Example 4	22	27.9	15	1.8	3.7	7.3	7.8	25	4.1	120

EXAMPLE 34-36

5 [0053] The invention relates to a preparation method of different shrinkage composite yarn, which is made from a porous spinneret. The arrangement of holes on the spinneret is elliptical, which means that the spinning hole center of the spinneret is located on a concentric ellipse. Concentric ellipse is a series of ellipses, all ellipses of the long axis collinear, and short axis collinear.

10 [0054] The arrangement of the orifices is long axis symmetry. The ratio of the length of the long axis to the short axis of the ellipse is 1.4, the spacing of the adjacent spinneret is equal to the diameter of the guide hole of the spinneret plus 1.7 mm, and the spinneret is a circular spinneret. The difference between the diameter of the circular spinneret and the maximum length of the long axis of the series is 12mm, the diameter of the spinneret is 1.8mm, the number of spinneret holes is 200, and the cross section shape of the spinneret spinning hole is diamond.

15 [0055] The modified polyester POY yarn is prepared by metering, squeezing, cooling, oiling and winding the modified polyester, and the modified polyester FDY yarn is prepared by metering, extrusion, cooling, oiling, drawing, heat setting and winding the modified polyester chips. The modified polyester POY yarn and the modified polyester FDY yarn are combined as the network structure to form the different shrinkage composite yarn. The main spinning process parameters are: spinning temperature 300°C, wind temperature 21 °C, combined network pressure 4.5bar, GR1 speed 800m/min, SR1 speed 3000m/min, GR2 speed 4000m/min, HT1 temperature 90°C, HT2 temperature 140°C, winding speed 3500m/min and the oil content of the different shrinkage composite yarn is 1.1%-1.2%. At the temperature of 90°C, the increasing rate of the space gap between the molecular chain inside the fiber and the data of mechanical properties of the fiber is:

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Table 3: the different shrinkage composite yarn's mechanical properties when use the polyester from EXAMPLE 5 to EXAMPLE 7

EXAMPLE	Modified polyester source	Breaking strength (cN/dtex)	Elongation at break (%)	Increased gap (v/v %)	Fiber density deviation rate (%)	CV value of breaking strength (%)	CV value of elongation at break (%)	CV value of curl shrinkage coefficient of variation (%)	Network degree (pieces/m)	Curl shrinkage rate(%)	Denier (dtex)
34	Example 5	2.3	30.4	10	1.1	2.8	6.7	6.9	15	3.1	120
35	Example 6	2.1	31.5	10	1.3	2.6	6.3	6.5	18	3.5	129
36	Example 7	2.4	30.9	10	1.4	2.9	6.0	62	20	2.7	125

EXAMPLES 37~39

5 [0056] The invention relates to a preparation method of different shrinkage composite yarn, which is made from a porous spinneret. The arrangement of holes on the spinneret is elliptical, which means that the spinning hole center of the spinneret is located on a concentric ellipse. Concentric ellipse is a series of ellipses, all ellipses of the long axis collinear, and short axis collinear.

10 [0057] The arrangement of the orifices is long axis symmetry. The ratio of the length of the long axis to the short axis of the ellipse is 1.4, the spacing of the adjacent spinneret is equal to the diameter of the guide hole of the spinneret plus 1.8mm, and the spinneret is a circular spinneret. The difference between the diameter of the circular spinneret and the maximum length of the long axis of the series is 13mm, the diameter of the spinneret is 2.5mm, the number of spinneret holes is 200, and the cross section shape of the spinneret spinning hole is straight line.

15 [0058] The modified polyester POY yarn is prepared by metering, squeezing, cooling, oiling and winding the modified polyester, and the modified polyester FDY yarn is prepared by metering, extrusion, cooling, oiling, drawing, heat setting and winding the modified polyester chips. The modified polyester POY yarn and the modified polyester FDY yarn are combined as the network structure to form the different shrinkage composite yarn. The main spinning process parameters are: spinning temperature 300°C, wind temperature 22 °C, combined network pressure 4 bar, GR1 speed 900m/min, SR1 speed 4200m/min, GR2 speed 4000m/min, HT1 temperature 115°C, HT2 temperature 135°C, winding speed 3500m/min and the oil content of the different shrinkage composite yarn is 1.0%-1.2%. At the temperature of 100°C, the increasing rate of the space gap between the molecular chain inside the fiber and the data of mechanical properties of the fiber is:

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Table 4: the different shrinkage composite yarn's mechanical properties when use the polyester from EXAMPLE 8 to EXAMPLE 10

EXAMPLE	Modified polyester source	Breaking strength (cN/dtex)	Elongation at break (%)	Increased gap(v/v gap %)	Fiber density deviation rate(%)	CVvalue of breaking strength (%)	CV value of elongation at break (%)	CV value of curl shrinkage coefficient of variation (%)	Network degree (pieces/m)	Curl shrinkage (%)	Denier (dtex)
37	Example 8	2.2	3 0.7	15	1.3	2.6	7.1	6.8	20	5.1	101
38	Example 9	2.4	3 3.0	15	1.1	2.1	7.2	6.4	17	5.5	105
39	Example 10	1.7	29.9	15	1.5	2.4	6.7	6.7	18	4.7	11 3

EXAMPLE 40~42

5 [0059] The invention relates to a preparation method of different shrinkage composite yarn, which is made from a porous spinneret. The arrangement of holes on the spinneret is elliptical, which means that the spinning hole center of the spinneret is located on a concentric ellipse. Concentric ellipse is a series of ellipses, all ellipses of the long axis collinear, and short axis collinear.

10 [0060] The arrangement of the orifices is long axis symmetry. The ratio of the length of the long axis to the short axis of the ellipse is 1.7, the spacing of the adjacent spinneret is equal to the diameter of the guide hole of the spinneret plus 1.9mm, and the spinneret is a circular spinneret. The difference between the diameter of the circular spinneret and the maximum length of the long axis of the series is 14mm, the diameter of the spinneret is 1.5mm, the number of spinneret holes is 210, and the cross section shape of the spinneret spinning hole is triangle.

15 [0061] The modified polyester POY yarn is prepared by metering, squeezing, cooling, oiling and winding the modified polyester, and the modified polyester FDY yarn is prepared by metering, extrusion, cooling, oiling, drawing, heat setting and winding the modified polyester chips. The modified polyester POY yarn and the modified polyester FDY yarn are combined as the network structure to form the different shrinkage composite yarn. The main spinning process parameters are: spinning temperature 290°C, wind temperature 22 °C, combined network pressure 4 bar, GR1 speed 900m/min, SR1 speed 4200m/min, GR2 speed 3500m/min, HT1 temperature 115°C, HT2 temperature 135°C, winding speed 3300m/min and the oil content of the different shrinkage composite yarn is 0.9%-1.1 %. At the temperature of 110°C, the increasing rate of the space gap between the molecular chain inside the fiber and the data of mechanical properties of the fiber is:

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Table 5: the different shrinkage composite yarn's mechanical properties when use the polyester from EXAMPLE 11 to EXAMPLE 13

EXAMPLE	Modified polyester source	Breaking strength (cN/dtex)	Elongation at break (%)	Increased gap(v/v gap %)	Fiber density deviation rate(%)	CVvalue of breaking strength (%)	CV value of elongation at break (%)	CV value of curl shrinkage coefficient of variation (%)	Network degree (pieces/m)	Curl shrinkage rate (%)	Denier (dtex)
40	Example 11	2.7	25 .0	18	1.4	3.1	6.8	6.4	22	3.1	145
41	Example 12	2.4	26.1	18	1.2	3.5	6.2	6.6	23	3.5	150
42	Example 13	2.6	27.3	18	1.0	3.6	6.6	6 .3	21	3.9	138

EXAMPLE 43-45

5 [0062] The invention relates to a preparation method of different shrinkage composite yarn, which is made from a porous spinneret. The arrangement of holes on the spinneret is elliptical, which means that the spinning hole center of the spinneret is located on a concentric ellipse. Concentric ellipse is a series of ellipses, all ellipses of the long axis collinear, and short axis collinear.

10 [0063] The arrangement of the orifices is long axis symmetry. The ratio of the length of the long axis to the short axis of the ellipse is 1.8, the spacing of the adjacent spinneret is equal to the diameter of the guide hole of the spinneret plus 1.5mm, and the spinneret is a circular spinneret. The difference between the diameter of the circular spinneret and the maximum length of the long axis of the series is 15mm, the diameter of the spinneret is 1.8mm, the number of spinneret holes is 240, and the cross section shape of the spinneret spinning hole is trilobal.

15 [0064] The modified polyester POY yarn is prepared by metering, squeezing, cooling, oiling and winding the modified polyester, and the modified polyester FDY yarn is prepared by metering, extrusion, cooling, oiling, drawing, heat setting and winding the modified polyester chips. The modified polyester POY yarn and the modified polyester FDY yarn are combined as the network structure to form the different shrinkage composite yarn. The main spinning process parameters are: spinning temperature 295°C, wind temperature 21°C, combined network pressure 3.8bar, GR1 speed 850m/min, SR1 speed 3500m/min, GR2 speed 3500m/min, HT1 temperature 115°C, HT2 temperature 135°C, winding speed 3300m/min and the oil content of the different shrinkage composite yarn is 0.8%-1.0%. At the temperature of 120°C, the increasing rate of the space gap between the molecular chain inside the fiber and the data of mechanical properties of the fiber is:

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Table 6: the different shrinkage composite yarn's mechanical properties when use the polyester from EXAMPLE 14 to EXAMPLE 16

EXAMPLE	Modified polyester source	Breaking strength (cN/dtex)	Elongation at break (%)	Increased gap(v/v gap %)	Fiber density deviation rate(%)	CVvalueof breaking strength (%)	CV value of elongation at break (%)	CV value of curl shrinkage coefficient of variation (%)	Network degree (pieces/m)	Curl shrinkage rate (%)	Denier (dtex)
43	Example 14	1.9	3 2.7	25	1.6	3.3	6. 3	6.1	21	1.9	110
44	Example 15	2.4	31.9	25	1.4	3.1	6. 7	5 .6	23	1.5	112
45	Example 16	2.1	35.0	25	1.7	2.6	6.9	5.7	24	2.6	115

EXAMPLE 46-49

5 [0065] The invention relates to a preparation method of different shrinkage composite yarn, which is made from a porous spinneret. The arrangement of holes on the spinneret is elliptical, which means that the spinning hole center of the spinneret is located on a concentric ellipse. Concentric ellipse is a series of ellipses, all ellipses of the long axis collinear, and short axis collinear.

10 [0066] The arrangement of the orifices is long axis symmetry. The ratio of the length of the long axis to the short axis of the ellipse is 1.8, the spacing of the adjacent spinneret is equal to the diameter of the guide hole of the spinneret plus 1.6mm, and the spinneret is a circular spinneret. The difference between the diameter of the circular spinneret and the maximum length of the long axis of the series is 16mm, the diameter of the spinneret is 2.2mm, the number of spinneret holes is 250, and the cross section shape of the spinneret spinning hole is hollow.

15 [0067] The modified polyester POY yarn is prepared by metering, squeezing, cooling, oiling and winding the modified polyester, and the modified polyester FDY yarn is prepared by metering, extrusion, cooling, oiling, drawing, heat setting and winding the modified polyester chips. The modified polyester POY yarn and the modified polyester FDY yarn are combined as the network structure to form the different shrinkage composite yarn. The main spinning process parameters are: spinning temperature 285°C, wind temperature 21°C, combined network pressure 3.8bar, GR1 speed 850m/min, SR1 speed 3500m/min, GR2 speed 3500m/min, HT1 temperature 95°C, HT2 temperature 138°C, winding speed 3600m/min and the oil content of the different shrinkage composite yarn is 0.9%-1.0%. At the temperature of 130°C, the increasing rate of the space gap between the molecular chain inside the fiber and the data of mechanical properties of the fiber is:

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Table 7. the different shrinkage composite yarn's mechanical properties when use the polyester from EXAMPLE 17 to EXAMPLE 20

EXAMPLE	Modified polyester source	Breaking strength (cN/dtex)	Elongation at break (%)	Increased gap(v/v gap %)	Fiber density deviation rate(%)	CVvalue of breaking strength (%)	CV value of elongation at break (%)	CV value of curl shrinkage coefficient of variation (%)	Network degree (pieces/m)	Curl shrinkage rate (%)	Denier (dtex)
46	Example 17	2.9	3 2.7	19	1.2	3.1	5. 9	6.2	23	4.1	132
47	Example 18	2.7	31.9	19	1.4	3.0	6.1	5.8	24	4.5	138
48	Example 19	2.6	30.6	19	1.5	2.6	6. 3	5.7	25	4.6	135
49	Example 20	2. 3	3 2.2	19	1.3	2.9	5.7	6.0	23	4.3	140

EXAMPLE 50~53

5 [0068] The invention relates to a preparation method of different shrinkage composite yarn, which is made from a porous spinneret. The arrangement of holes on the spinneret is elliptical, which means that the spinning hole center of the spinneret is located on a concentric ellipse. Concentric ellipse is a series of ellipses, all ellipses of the long axis collinear, and short axis collinear.

10 [0069] The arrangement of the orifices is long axis symmetry. The ratio of the length of the long axis to the short axis of the ellipse is 1.8, the spacing of the adjacent spinneret is equal to the diameter of the guide hole of the spinneret plus 1.8mm, and the spinneret is a circular spinneret. The difference between the diameter of the circular spinneret and the maximum length of the long axis of the series is 15mm, the diameter of the spinneret is 2.5mm, the number of spinneret holes is 260, and the cross section shape of the spinneret spinning hole is flat.

15 [0070] The modified polyester POY yarn is prepared by metering, squeezing, cooling, oiling and winding the modified polyester, and the modified polyester FDY yarn is prepared by metering, extrusion, cooling, oiling, drawing, heat setting and winding the modified polyester chips. The modified polyester POY yarn and the modified polyester FDY yarn are combined as the network structure to form the different shrinkage composite yarn. The main spinning process parameters are: spinning temperature 285°C, wind temperature 21°C, combined network pressure 4.2bar, GR1 speed 950m/min, SR1 speed 3800m/min, GR2 speed 3600m/min, HT1 temperature 95°C, HT2 temperature 138°C, winding speed 3600m/min and the oil content of the different shrinkage composite yarn is 0.9%-1.0%. At the temperature of 100°C, the increasing rate of the space gap between the molecular chain inside the fiber and the data of mechanical properties of the fiber is:

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Table 8: the different shrinkage composite yarn's mechanical properties when use the polyester from EXAMPLE 21 to EXAMPLE 24

EXAMPLE	Modified polyester source	Breaking strength (cN/dtex)	Elongation at break (%)	Increased gap (v/v%)	Fiber density deviation rate (%)	CV value of breaking strength (%)	CV value of elongation at break (%)	CV value of curl shrinkage coefficient of variation (%)	Network degree (pieces/m)	Curl shrinkage rate (%)	Denier (dtex)
50	Example 21	2.1	31.7	15	1.4	3.4	6.2	6.1	20	4.3	121
51	Example 22	2.7	31.9	15	1.1	3.1	6.4	5.9	22	4.5	127
52	Example 23	2.6	31.6	15	1.3	2.9	6.1	5.7	24	4.1	129
53	Example 24	2.3	32.2	15	1.1	3.3	5.9	6.0	22	4.7	119

EXAMPLE 54 ~ 57

5 [0071] The invention relates to a preparation method of different shrinkage composite yarn, which is made from a porous spinneret. The arrangement of holes on the spinneret is elliptical, which means that the spinning hole center of the spinneret is located on a concentric ellipse. Concentric ellipse is a series of ellipses, all ellipses of the long axis collinear, and short axis collinear.

10 [0072] The arrangement of the orifices is long axis symmetry. The ratio of the length of the long axis to the short axis of the ellipse is 1.8, the spacing of the adjacent spinneret is equal to the diameter of the guide hole of the spinneret plus 1.5mm, and the spinneret is a circular spinneret. The difference between the diameter of the circular spinneret and the maximum length of the long axis of the series is 16mm, the diameter of the spinneret is 1.8mm, the number of spinneret holes is 300, and the cross section shape of the spinneret spinning hole is hollow.

15 [0073] The modified polyester POY yarn is prepared by metering, squeezing, cooling, oiling and winding the modified polyester, and the modified polyester FDY yarn is prepared by metering, extrusion, cooling, oiling, drawing, heat setting and winding the modified polyester chips. The modified polyester POY yarn and the modified polyester FDY yarn are combined as the network structure to form the different shrinkage composite yarn. The main spinning process parameters are: spinning temperature 288°C, wind temperature 21°C, combined network pressure 4.2bar, GR1 speed 950m/min, SR1 speed 4200m/min, GR2 speed 3600m/min, HT1 temperature 110°C, HT2 temperature 138°C, winding speed 3800m/min and the oil content of the different shrinkage composite yarn is 0.9%-1.1%. At the temperature of 120°C, the increasing rate of the space gap between the molecular chain inside the fiber and the data of mechanical properties of the fiber is:

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Table 9. the different shrinkage composite yarn's mechanical properties when use the polyester from EXAMPLE 25 to EXAMPLE 28

EXAMPLE	Modified polyester source	Breaking strength (cN/dtex)	Elongation at break (%)	Increased gap (v/v%)	Fiber density deviation rate (%)	CV value of breaking strength (%)	CV value of elongation at break (%)	CV value of curl shrinkage coefficient of variation (%)	Network degree (pieces/m)	Curl shrinkage rate (%)	Denier (dtex)
54	Example 25	2.3	32.7	30	1.0	3.0	6.0	5.6	15	4.7	138
55	Example 26	1.9	31.9	30	0.9	3.1	5.4	5.9	17	4.9	141
56	Example 27	2.1	33.0	30	1.1	2.7	5.7	5.7	23	4.2	150
57	Example 28	2.5	32.2	30	1.3	3.3	5.9	6.0	20	4.5	147

EXAMPLE 58

[0074] Dyeing process of different shrinkage composite yarn:

The different shrinkage composite yarn prepared in Example 29 is dyed in a high temperature and high pressure machine under the following conditions: before dyeing, the different shrinkage composite yarn is treated with a nonionic surfactant at 60°C for 30 minutes, and then added to the dyeing solution. In the dyeing solution, the disperse dye content is 2.0%(o.w.f). The dispersant is NNO. The concentration of dispersant NNO is 1.2g/L and the pH value is 5, the bath ratio is 1:50. Dye the yarn at 60 °C, and then raise the temperature to 90°C, 100°C, 110°C, 120°C and 130°C, dye at each temperature for 1 hour.

[0075] Dye the common fibers under the same dyeing conditions. The percentage of dyeing of the modified polyester fiber after dyeing is obtained by the following method:

The percentage of dyeing is determined by the residual liquid colorimetric method. Take the appropriate amount of dyeing stock solution and dyeing residue, and add N, N-2 methylformamide (DMF) and distilled water. The ratio of DMF to water in the dye solution is 70/30 (v/v), the absorbance of the dye solution is measured by an ultraviolet - visible spectrophotometer, and the percentage of dyeing is calculated by the following formula.

$$\text{Percentage of dyeing} = 100 \% \times \left(1 - \frac{A_1}{A_0} \right)$$

[0076] In the formula above, A0 and A1 are respectively the absorbances of the dyeing stock solution and the dye residue.

[0077] When the disperse dye is disperse red 3B, disperse blue SE-2R or disperse turquoise S-GL, the dyeing percentage of different shrinkage composite yarn and the common fiber is as follows:

Table 10: the comparison of the percentage of dyeing between different shrinkage composite yarn and ordinary fiber when use modified polyester prepared in EXAMPLE 29

Percentage of dyeing	temperature	90 °C	100 °C	110 °C	120 °C	130 °C
Disperse red 3B	Different shrinkage composite yarn	50.3	77.3	84.2	88.0	89.4
	Ordinary fiber	28.2	46.3	78.5	81.7	90.2
Disperse blue SE-2R	Different shrinkage composite yarn	53.6	78.7	84.4	86.4	89.1
	Ordinary fiber	12.3	35.2	73.4	88.9	91.3
Scattered turquoise blue S-GL	Different shrinkage composite yarn	44.8	70.4	76.0	83.7	86.7
	Ordinary fiber	11.8	36.3	70.9	75.6	82.6

[0078] By comparing the dyeing effect of the different shrinkage composite yarn with the ordinary fiber, it can be seen that the dyeing effect of the different shrinkage composite yarn is obviously superior to that of the ordinary fiber, and it can also be seen that the branched diol segment in the macromolecule of the modified polyester prepared in the invention, making the rate of increase much greater than the free volume unbranched general properties of the polyester of the macromolecular chains. The increase of the free volume helps fine particles go into the interior of the polyester, the free volume of the polyester fiber made from the modified polyester is much larger than that of the unbranched ordinary polyester fiber at the same temperature, which increases the diffusion degree of the dye and improves the dyeing property of the polyester fiber.

EXAMPLE 59

[0079] Dyeing process of different shrinkage composite yarn:

The different shrinkage composite yarn prepared in Example 31 is dyed in a high temperature and high pressure machine under the following conditions: before dyeing, the different shrinkage composite yarn is treated with a nonionic surfactant at 60°C for 30 minutes, and then added to the dyeing solution. In the dyeing solution, the disperse dye content is 2.0%(o.w.f). The dispersant is NNO. The concentration of dispersant NNO is 1.2g/L and the pH value is 5, the bath

ratio is 1:50. Dye the yarn at 60 °C , and then raise the temperature to 90°C, 100°C, 110°C, 120°C and 130°C, dye at each temperature for 1 hour.

[0080] Dye the common fibers under the same dyeing conditions. The percentage of dyeing of the modified polyester fiber after dyeing is obtained by the following method:

The percentage of dyeing is determined by the residual liquid colorimetric method. Take the appropriate amount of dyeing stock solution and dyeing residue, and add N, N-2 methylformamide (DMF) and distilled water. The ratio of DMF to water in the dye solution is 70/30 (v/v), the absorbance of the dye solution is measured by an ultraviolet - visible spectrophotometer, and the percentage of dyeing is calculated by the following formula.

$$\text{Percentage of dyeing} = 100 \% \times \left(1 - \frac{A_1}{A_0} \right)$$

[0081] In the formula above, A0 and A1 are respectively the absorbances of the dyeing stock solution and the dye residue.

[0082] When the disperse dye is disperse red 3B, disperse blue SE-2R or disperse turquoise S-GL , the percentage of dyeing percentage of different shrinkage composite yarn and the common fiber is as follows:

Table 11: the comparison of the percentage of dyeing between different shrinkage composite yarn and ordinary fiber when use modified polyester prepared in EXAMPLE 31

dye	temperature	90 °C	100 °C	110 °C	120 °C	130 °C
Disperse red 3B	Different shrinkage composite yarn	50.3	77.3	84.2	88.0	89.4
	Common fiber	28.2	46.3	78.5	81.7	90.2
Disperse blue SE-2R	Different shrinkage composite yarn	53.6	78.7	84.4	86.4	89.1
	Common fiber	12.3	35.2	73.4	88.9	91.3
Scattered turquoise blue S-GL	Different shrinkage composite yarn	44.8	70.4	76.0	83.7	86.7
	Common fiber	11.8	36.3	70.9	75.6	82.6

[0083] By comparing the dyeing effect of the different shrinkage composite yarn with the ordinary fiber, it can be seen that the dyeing effect of the different shrinkage composite yarn is obviously superior to that of the ordinary fiber, and it can also be seen that the branched diol segment in the macromolecule of the modified polyester prepared in the invention, making the rate of increase much greater than the free volume unbranched general properties of the polyester of the macromolecular chains. The increase of the free volume helps fine particles go into the interior of the polyester , the free volume of the polyester fiber made from the modified polyester is much larger than that of the unbranched ordinary polyester fiber at the same temperature, which increases the diffusion degree of the dye and improves the dyeing property of the polyester fiber.

Claims

1. This invention relates to a different shrinkage composite yarn, wherein the material of the different shrinkage composite yarn is a modified polyester, and the modified polyester is composed of a terephthalic acid chain, an ethylene glycol chain and a diol chain containing a branched chain; the branched diol segment locates on a non-terminal carbon in the diol chain segment and the branched chain is a diol chain segment containing a straight chain carbon chain of 5-10 carbon atoms; the size of the different shrinkage composite yarn is 100-150 dtex. the breaking strength is ≥ 1.9 CN / dtex, the elongation at break is 30.0 ± 5.0 ; at the temperature of 80°C-130°C, the space gap between molecular chains in the fiber increased by 10-30v/v%; the deviation rate of fiber density of the different shrinkage composite yarn is $\leq 2.0\%$; the CV value of breaking strength is $\leq 4.0\%$, and the CV value of elongation at break is $\leq 8.0\%$, and the CV value of coiling shrinkage coefficient of variation is $\leq 8.0\%$, and crimp shrinkage is $3.50 \pm 2.0\%$, and the oil content is $1.0 \pm 0.2\%$, network 20 ± 5 units/m; the increase of the space gap between the molecular chains refers to the comparison of the spatial gaps between molecular chains at the same temperature between modified polyester and common polyester.

2. According to Claim 1, a preparation method of a different shrinkage composite yarn, wherein the modified polyester is spun from a porous spinneret to produce a different shrinkage composite yarn, and the arrangement of the spinneret holes in the porous spinneret is an elliptical arrangement; the elliptical arrangement means that the center of the spinning hole of the spinneret is located on the concentric ellipse, the concentric ellipse is a series of ellipses, the long axis collinear of all the ellipses, and the short axis collinear; the preparation method of the different shrinkage composite yarn is as follows: the modified polyester POY yarn is prepared by metering, squeezing, cooling, oiling and winding the modified polyester, and the modified polyester FDY yarn is prepared by metering, extrusion, cooling, oiling, drawing, heat setting and winding the modified polyester chips; the modified polyester POY yarn and the modified polyester FDY yarn are combined as the network structure to form the different shrinkage composite yarn; the preparation steps of the modified polyester are as follows:

(1) preparation of terephthalic acid glycol ester:

mix terephthalic acid and branched diol to slurry, and carry out the esterification reaction under the catalytic action of concentrated sulfuric acid to obtain a terephthalic acid glycol ester; the branched diol refers to a diol having a branched chain which is a non-terminal carbon in the diol segment and a branched chain having a linear carbon chain of 5 to 10 carbon atoms;

(2) preparation of ethylene terephthalate:

mix the terephthalic acid and the ethylene glycol to slurry, carry out the esterification reaction to obtain ethylene terephthalate.

(3) preparation of modified polyester:

after the esterification reaction in the step (2) is completed, add the terephthalic acid glycol ester prepared in the step (1), stir and mix, run the polycondensation reaction under the action of the catalyst and the stabilizer, and under the condition of the negative pressure. First in a low vacuum stage and then in a high vacuum stage to obtain a modified polyester.

3. According to Claim 2, a preparation method of a different shrinkage composite yarn, wherein the specific preparation steps of the modified polyester are as follows:

(1) preparation of terephthalic acid glycol ester:

add the slurry of the terephthalic acid and the branched diol to the reactor, and carry out the esterification reaction under the catalytic action of concentrated sulfuric acid; the esterification reaction is carried out under a pressurized nitrogen environment, and the pressure is normal pressure to 0.3 MPa, and the temperature is 180-240 °C; the reaction ends when the water distillation amount in the esterification reaction reaches 90% of the theoretical value or more than that. Then the terephthalic acid glycol ester is obtained;

(2) preparation of ethylene terephthalate:

add the slurry of the terephthalic acid and ethylene glycol into a reactor and then carry out the esterification reaction; the esterification reaction is carried out under a pressurized nitrogen environment, and the pressure is normal pressure to 0.3 MPa, and the temperature is 250-260 °C; the reaction ends when the water distillation amount in the esterification reaction reaches 90% of the theoretical value or more than that; then the ethylene terephthalate is obtained.

(3) preparation of modified polyester:

after the end of the esterification reaction in the step (2), add the terephthalic acid glycol ester prepared in the step (1), stir and mix for 15-20 minutes under the action of the catalyst and the stabilizer, and a negative pressure; carry out the polycondensation reaction under the condition of the low-vacuum stage, the pressure is smoothly pumped from normal pressure to an absolute pressure under 500Pa, the temperature is controlled at 260~270°C, and the reaction time is 30~50 minutes; then turn to high vacuum stage, the polycondensation reaction continues and the reaction pressure is reduced to an absolute pressure of less than 100 Pa, and the reaction temperature is controlled at 275 to 280 °C, and the reaction time is 50 to 90 minutes in order to obtain a modified polyester;

the main spinning process parameters of the different shrinkage composite yarn are as follows:

Spinning temperature: 280-300°C;

Wind temperature: 20-22 °C;

Network pressure of joint stock: 3.5-4.5bar.

GR1 speed: 800-1000m/min;

SR1 speed: 3000-4200m/min;

GR2 speed: 3000-4000m/min;

HT1 temperature: 90-115°C;

HT2 temperature: 130-140°C;

Winding speed: 3000-4000m/min.

4. According to Claim 2, a method for preparing a different shrinkage composite yarn, wherein, in step (1), the molar ratio of terephthalic acid to branched diol is 1: 1.3-1.5; the amount of concentrated sulfuric acid added is 0.3-0.5% of the weight of terephthalic acid; The concentration of concentrated sulfuric acid is 50-60 wt%;
in step (2), the molar ratio of terephthalic acid to ethylene glycol is 1: 1.2-2.0;
in step (3), the molar percentage value of the diol terephthalate and ethylene terephthalate is 2-5%; the catalyst is antimony trioxide, antimony glycol or antimony acetate, and the amount of catalyst added ranges from 0.01%-0.05% of the total weight of terephthalic acid; the stabilizer is triphenyl phosphate, trimethyl phosphate or trimethyl phosphite, and the amount of stabilizer added ranges from 0.01%-0.05% of the total weight of terephthalic acid; the number average molecular weight of the modified polyester ranges from 15000-30000.
5. A method of preparation of the different shrinkage composite yarn according to Claim 2, wherein the branched diol is one or more items chosen from the group consisting of a 2-pentyl-1,3 propanediol, a 2-hexyl-1,3 propanediol, a 2-heptyl-1,3 propanediol, a 2-octyl-1,3 propanediol, a 2-mercapto-1,3 propanediol, a 2-mercapto group-1,3 propanediol, a 2-pentyl-1,4 butanediol, a 2-hexyl-1,4 butanediol, a 2-heptyl-1,4 butanediol, a 2-octyl-1,4 butanediol, a 2-mercapto-1,4 butanediol, a 2-mercapto-1,4 butanediol, a 2-pentyl-1,5 pentanediol, a 2-hexyl-1,5-pentanediol, a 2-heptyl-1,5-pentanediol, a 2-octyl-1,5-pentanediol, a 2-mercapto group-1,5 pentanediol glycol, a 2-mercapto-1,5 pentanediol, a 2-pentyl-1,6 hexanediol segment, a 2-hexyl-1,6 hexanediol, a 2-heptyl-1,6-hexanediol, a 2-octyl-1,6-hexanediol, a 2-mercapto-1,6-hexanediol and a 2-mercapto-1,6 hexanediol.
6. A method of preparation of the different shrinkage composite yarn according to Claim 2, wherein the arrangement of the spinneret holes is long axis and/or short axis symmetry.
7. A method of preparation of the different shrinkage composite yarn according to Claim 2, wherein the ratio of the long axis of the ellipse to the length of the short axis is 1.3-1.8; the spacing of the adjacent spinneret holes is greater than the diameter of the guide hole equal to the diameter of the guide hole of the spinneret hole plus 1.5mm.
8. A method of preparation of the different shrinkage composite yarn according to Claim 2, wherein the spinneret is a circular spinneret or an elliptical spinneret; the difference between the diameter of the circular spinneret and the maximum length of the long axis of the series ellipse is greater than 10 mm, and the difference value between the elliptical spinneret and the maximum length of the long axis of the series ellipse is greater than 10mm.
9. A method of preparation of the different shrinkage composite yarn according to Claim 2, wherein the guide hole diameter of the spinneret is 1.5-2.5mm; the number of spinneret holes is greater than or equal to 192.
10. A method of preparation of the different shrinkage composite yarn according to Claim 2, wherein the cross-section shape of the spinneret spinning hole is one kind of circular, square, diamond, one font, triangular, trilobal, hollow or flat.

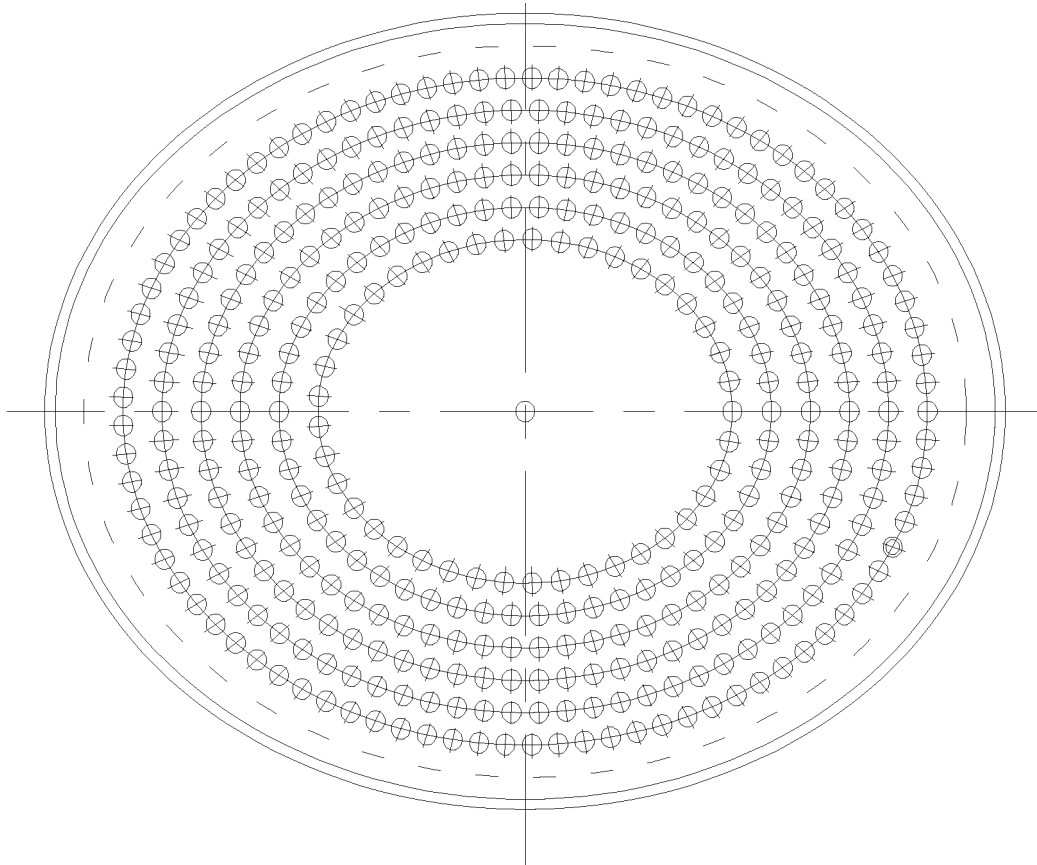


Fig.1

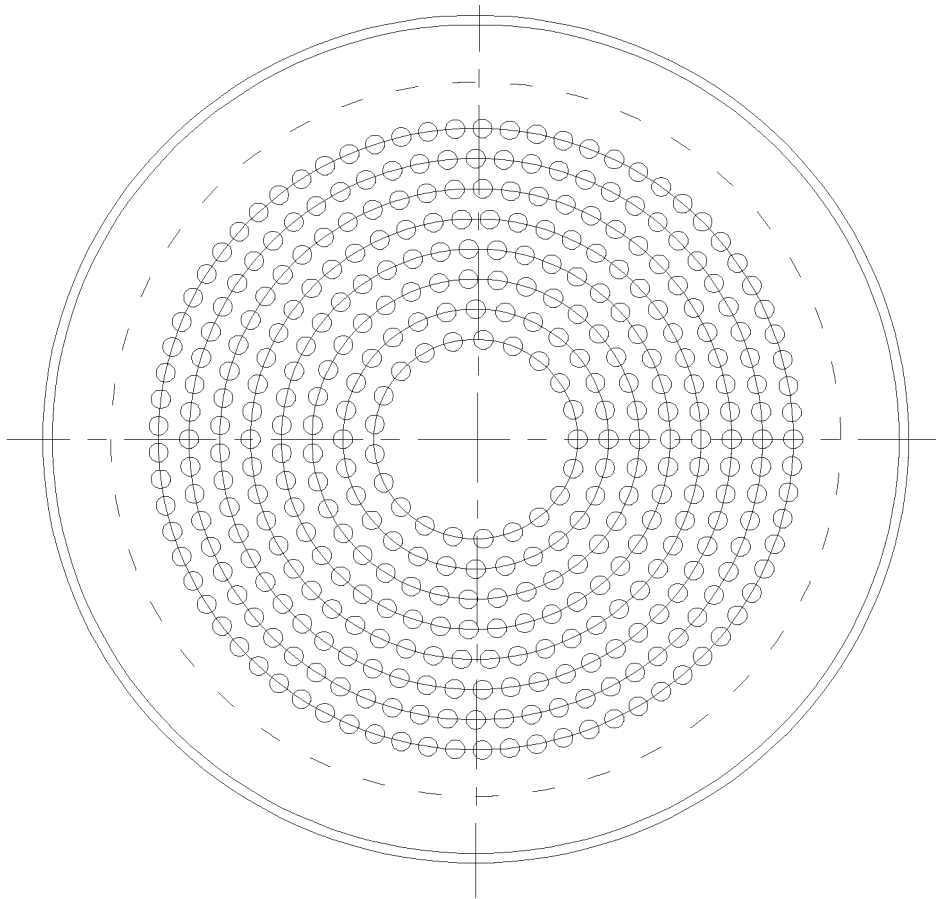


Fig. 2

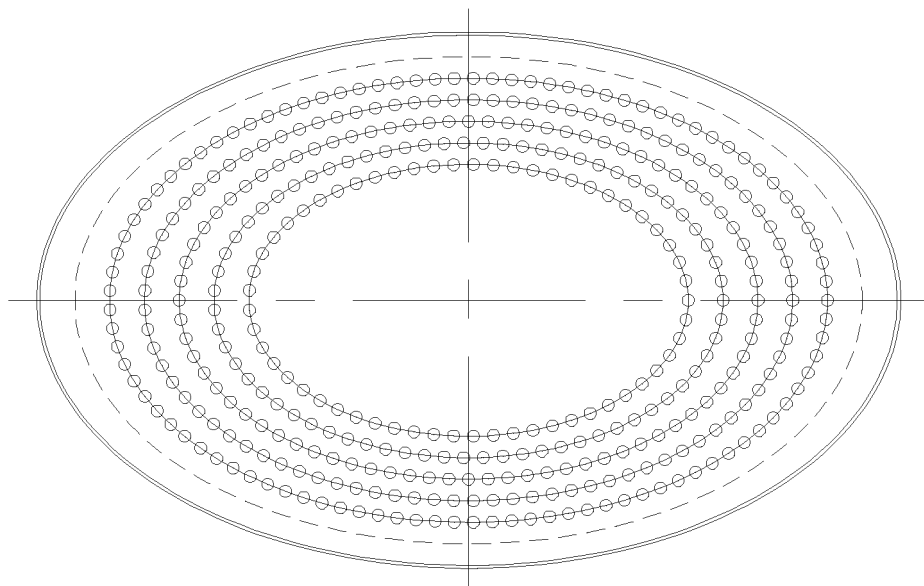


Fig. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2017/089945

A. CLASSIFICATION OF SUBJECT MATTER

D01F 6/92 (2006.01) i; D01F 1/10 (2006.01) i; D01D 4/02 (2006.01) i; D01D 5/08 (2006.01) i; D01D 5/253 (2006.01) i; D01D 5/24 (2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

D01F, D01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNKI, CNABS, CNTXT, WPI, EPODOC, ISI web of knowledge: 聚酯, 涤纶, 对苯二甲酸, 侧链, 支链, 二元醇, 二醇, 戊基, 己基, 辛基, 壬基, 庚基, 癸基, 喷丝板, 椭圆, PET, polyester, branched chain, side chain, diol, dibastic alcohol, divalent alcohol, diatomic alcohol, dihydric alcohol

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
PX	CN 106381558 A (JIANGSU HENGLI CHEMICAL FIBER CO., LTD.), 08 February 2017 (08.02.2017), claims 1-10	1-10
X	CN 102648231 A (TORAY FIBERS & TEXTILES RESEARCH LABORATORIES (CHINA) CO., LTD.), 22 August 2012 (22.08.2012), description, page 2, lines 6-13, and embodiment 1	1
Y	CN 102648231 A (TORAY FIBERS & TEXTILES RESEARCH LABORATORIES (CHINA) CO., LTD.), 22 August 2012 (22.08.2012), description, page 2, lines 6-13, and embodiment 1	2-10
Y	CN 102851757 A (JIANGSU HUAYA FIBER CO., LTD.), 02 January 2013 (02.01.2013), description, paragraphs [0007]-[0013], and figure 1	2-10
A	CN 104878487 A (JIANGSU HENGLI CHEMICAL FIBER CO., LTD.), 02 September 2015 (02.09.2015), entire document	1-10
A	CN 101063236 A (DONGHUA UNIVERSITY), 31 October 2007 (31.10.2007), entire document	1-10
A	JP 2014189933 A (TORAY INDUSTRIES), 06 October 2014 (06.10.2014), entire document	1-10

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	"&" document member of the same patent family

Date of the actual completion of the international search 19 September 2017	Date of mailing of the international search report 26 September 2017
Name and mailing address of the ISA State Intellectual Property Office of the P. R. China No. 6, Xitucheng Road, Jimenqiao Haidian District, Beijing 100088, China Facsimile No. (86-10) 62019451	Authorized officer SONG, Lin Telephone No. (86-10) 62084562

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT
 Information on patent family members

 International application No.
 PCT/CN2017/089945

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
CN 106381558 A	08 February 2017	None	
CN 102648231 A	22 August 2012	CN 102030893 A	27 April 2011
		WO 2011038671 A1	07 April 2011
		KR 20120088731 A	08 August 2012
		JP 2013506039 A	21 February 2013
		US 2012202964 A1	09 August 2012
		JP 5720059 B2	20 May 2015
		KR 101739402 B1	24 May 2017
CN 102851757 A	02 January 2013	None	
CN 104878487 A	02 September 2015	CN 104878487 B	12 April 2017
CN 101063236 A	31 October 2007	CN 100567600 C	09 December 2009
JP 2014189933 A	06 October 2014	None	

Form PCT/ISA/210 (patent family annex) (July 2009)